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MAGNETIC STUDY OF IRON-CONTAINING GLASSES AT LOW TEMPERATURE

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ABSTRACT. This paper deals with the low temperature magnetic property of several iron glasses. The value of the square of the magnetic moment of iron at different temperatures in the liquid oxygen range has been determined. In almost all cases this value is found to decrease with decreasing temperature. The variation of the moments with temperature is dependent on the composition of the glass. These findings have been discussed from the point of view of the glass structure.

INTRODUCTION

In a previous paper by the author (1959) on the magnetic study of iron glasses at room temperature, it was suggested that the electrovalent and covalent forms of iron can both exist simultaneously along with the collodial oxides of iron in the same glass system. In the course of the investigation on the magnetic property of iron glass at room temperature, the evidence for the presence of ferromagnetic component in any glass system has not been observed. It was however expected that similar studies at low temperature may yield more fruitful results.

EXPERIMENTAL

Iron glasses of boric oxide, soda-boric oxide, potash-boric oxide, lithia-boric oxide and high lead-silica glass bases respectively were selected for the present study. Details of the method of preparation and analysis are given in the previous paper by the author (1959).

In the case of low temperature measurement at any desired temperature in the liquid oxygen range, a cryostatic arrangement of the gas-flow type originally designed by Bose (1947) and recently modified by Dutta Roy (1955) was used. The cryostatic chamber is cooled by the flow of cold air through it obtained by the evaporation of liquid oxygen at the bottom of the chamber. The efficiency of cooling and the steadiness of the temperature is ensured by packing the chamber with copper gauze which furnishes heat exchange in the system. An automatic relay system controlled by a constant volume air thermometer drives a suction pump and regulates the flow of cold air.

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The experimental glass specimens consisted of a number of samples of different compositions prepared under neutral, reducing or oxidising conditions including one set of high potash content (K_2O = 41.40%) potash-boric oxide glass prepared in both neutral and reduced conditions. The colour of the oxidised and neutral glasses were yellow, while that of the reduced glass was bluish green. The variation of the square of the effective moment value (p^2_{eff}) of each specimen from room temperature to 100° K is given in the Figure 1, where ordinate on the

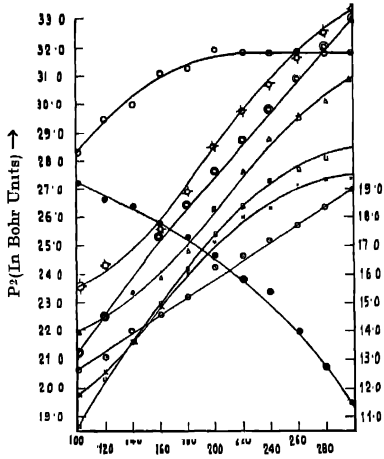

Fig. 1.

- ⊙ Soda-Boric oxide (neutral) Na_2O = 9·475%; Fe = 2 8
- Δ Soda-Boric oxide (reduced) Na_2O = 31·0%; Fe = 1·210%
- □ Potash-Boric oxide (neutral) K_2O = 14 2%; Fe = 1·673%
- O Potash-Boric oxide (neutral) K_2O = 41·4%; Fe = 1·221%
- × Potash-Boric oxide (reduced) K_2O = 41·4%; Fe= 1·221%
- @ Lithia-Boric oxide (neutral) Li_2O = 31·2%; Fe = 0·25%
- ★ Lead Oxide-Potash Silica (oxidised) PbO=60%; K_2O=10%; Fe=0·78%
- ● Boric oxide Fe = 0·2712%

left represents the effective mean square moments p_{eff}^2, in Bohr units for alkali-boric oxide and lead oxide-potash silica glasses, while the ordinate on the right is p^2_{eff} for boric oxide glass; the abscissa represents the temperature on Kelvin scale.

DISCUSSION

From a critical analysis of the experimental results it is quite evident that though in most cases the room temperature values of p^2_{eff} lie in between the ferric

and ferrous ion values (with the exception of the boric oxide glass which has been dealt with separately later on), they decrease with decreasing temperature and even drop down below the ferrous 'spin-only' value. The comparative values of p^2_{eff} at several temperatures between 300°K and 100°K of each glass are shown in the following table.

TABLE I

Description of glass	Composition in weight percent	Iron in weight percent	P^2_{eff} values at 300°K	240°K	200°K	160°K	100°K
Soda-boric oxide (neutral)	Na_2O = 9.475	2.848	27.00	25 15	23.75	22.65	20.65
Soda-boric oxide (reduced)	Na_2O = 31 0	1.210	31 45	28 65	26.40	24.10	22.00
Potash-boric oxide (neutral)	K_2O = 14.2	1.673	28.50	27.40	25 50	23.00	18.65
Potash-boric oxide (neutral)	K_2O = 41 4	1 221	31.85	31 85	32.00	31 40	28.25
Potash-boric oxide (reduced)	K_2O = 41 4	1 221	27.39	26 79	25.21	22.92	19.84
Lithia-boric oxide (neutral)	Li_2O = 31.2	0 2500	33.00	29 76	27.58	25 56	21.12
High lead-potash-silica (oxidised)	K_2O = 10.0, PbO = 60 0	0 780	33 35	30.78	28.42	25.85	23 43

The deviation in each case from the standard Fe^{+3} and Fe^{+2} (spin-only) value can be readily observed if we consider the theoretical p^2 values of these two ions: p^2 for Fe^{+3} = 35.04; p^2 for Fe^{+2} (spin-only) = 24.01 in terms of the Bohr unit.

For the sake of comparison the p^2_{eff}—T data for two typical ionic salts of iron are quoted below :

TABLE II

$Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, $24H_2O$ (Dutta-Ray[3], 1955)		$FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$ (Bose[4], 1948)	
Temp.°K	p^2_{eff}	Temp.°K	p^2_{eff}
300.5	35.08	296.8	28.49
278 8	35.06	182.5	28.57
242 0	35.07	84.8	27.13
222.1	35.05		
195.5	34.84		
179 2	34.81		
171.2	34 74		
147.8	34.83		
133.2	34.92		
121.0	35.00		
99.0	34 91		

It is quite evident from the preceding p^2_{eff} data for the electrovalent iron compounds that the variation of the p^2_{eff} values with lowering temperature is small. In contrast with this the decreasing trend of the p^2_{eff} values at low temperatures in the case of glass specimens is quite prominent.

In the multicomponent paramagnetic carriers of iron glass the mean moment of iron in the glass is due to the contribution of the moment values of the several magnetic carriers. The effective moment value of iron in glass and its behaviour towards low temperature will depend on the state of existence and proportion of the different forms of iron which again are interrelated with the glass composition, the method of preparation and working conditions. In the present set of samples, the deviation from the straight line nature of the p^2_{eff}—T curves with respect to T axis at the low temperature region increases in the following order :

$K_2O(41.4)-B_2O_3(N)$, $K_2O(41.4)-B_2O_3(R)$, $K_2O(14.2)-B_2O_3(N)$, Na_2O $(9.475)-B_2O_3(N)$, $Na_2O(31.0)-B_2O_3(R)$, $Li_2O(31.2)-B_2O_3(N)$, $PbO(60.0)-K_2O(10.0)-SiO_2(O)$

Where (N) = Neutral glass
(R) = Reduced glass
and (O) = Oxidised glass

It is thus clear that there is no simple relation between the abnormally low p^2_{eff} values at low temperatures and those at room temperature of iron in the glass. For example, at room temperature the p^2_{eff} value of iron in high lead silica glass ($p^2_{eff} = 33.35$) is greater than iron in high potash ($p^2_{eff} = 31.85$; $41.4\%K_2O$) boric oxide glass but deviation from the straight line relation of p^2_{eff} —T curve is much greater in high lead silica glass than in the above potash

The decreasing trend of the p^2_{eff} values with the lowering of temperature may be due to the single or combined effects of the following factors : (1) the covalent nature of the linkage of some forms of liquid phase colouring iron complexes; (2) anomalous low temperature behaviour of some solid phase iron colouring centres, if there be any in the glassy matrix; and (3) a gradual change of the glass structure with the lowering of temperature, in which case a change in the distribution and nature of the electronic linkage in some forms of iron, particularly of the liquid phase colours, takes place.

It is well known that the nature of the chemical bonding, valency, etc. of a paramagnetic substance is directly related to its paramagnetic moment value. Mention has been made by Guha (1951) of some compounds of iron where the moment value (p) of iron decreases considerably with the lowering of temperature,

e.g. $K_3Fe_3(CN)_6$, $FeSO_4.7H_2O$ (Guha, 1951), etc. The p^2_{eff} —T values of these substances are quoted in the following table

TABLE III

$K_3Fe(CN)_6$		$FeSO_4, 7H_2O$	
Temp.°K	p^2_{eff}	Temp.°K	p^2_{eff}
304.9	5 077	303.1	26.76
254.9	4.871	241.9	26.42
226.0	4.656	186.3	25.41
193.9	4 546	139.6	24 58
156.9	4.216	107.4	23.60
123.6	3 962	82.0	22.90
81.1	3.631		

It is quite evident from the above table that in $K_3Fe(CN)_6$ (the covalent compound) ferric iron has a moment of 2.25 B.M. at room temperature, a little higher than the 'spin only' value for one unpaired electron. Moreover, the moment square value of iron in that compound decreases to about 1.9 B.M. at 81.1°K with the lowering of temperature. Similar is the case with $FeSO_4.7H_2O$ (though to a smaller extent) where the room temperature value corresponds satisfactorily to the 'spin only' value with some orbital contribution for the Fe (ous) ion in the ionic compound, but the value decreases with the decrease of temperature even below the 'spin only' value. Thus from the consideration of the above results of the covalent ferric compound and of the ionic ferrous salt, it is suggested that some of the paramagnetic carriers of iron glass may behave similarly towards low temperature, especially those (iron complexes) with covalent linkage. Again, the rate of decrease of the p^2_{eff} value with temperature is connected with the glass composition, for the rate of fall in lithia-boric oxide and high lead-silica glasses is higher than in the potash-boric oxide glasses.

Thus it is observed that the decrease with temperature of the p^2_{eff} value in almost all the glasses resembles very much the behaviour of Fe^{+3} ion in the covalent compound of ferricynide, but the moment square values of iron at room temperature remain always very high, although somewhat lower than the ferric 'spin only' value. The resultant behaviour of iron glass depends on the percentage composition of different forms of Fe^{+2} and Fe^{+3} in different stages of bonding.

It has been stated before that some other factors, such as the low temperature magnetic property of some solid phase colours, e.g. oxides of iron and low temperature glass structure are worth considering for the peculiar low temperature behaviour of iron glass.

Among the possible forms of solid phase colours, the presence of α-Fe_2O_3 and Fe_3O_4 has been suggested by Moore and his coworkers (1949 and 1951). The absence of any ferromagnetic component like Fe_3O_4 in the glass is shown in the previous paper by the author (1959). Consequently, if at all any ferromagnetic component is present, its particle size must be lower than the magnetic domain size, in which case it can exhibit only strong paramagnetism with complicated dependence on temperature. The Moore school of workers assigns susceptibility values $\chi_m = 39.4 \times 10^{-6}$ for α-Fe_2O_3 and $\chi_m = 424 \times 10^{-6}$ for Fe_3O_4 at 20°C [Abou-El-Azm (1954)]. The change in the magnetic behaviour of those oxides in a finely divided state of varying particle size with the lowering of temperature promises to be an interesting problem of study. In the massive form, χ_m for α-Fe_2O_3 is independent of temperature and again the moment value of α-Fe_2O_3 is related to the particle size [Chevallier *et al* (1937)].

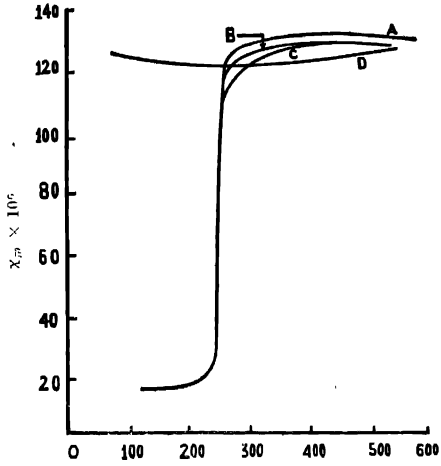

Fig. 2.

A → Pure α-Fe_2O_3

B → α-Fe_2O_3 + 0.2 T_t

C → α-Fe_2O_3 + 0.5 T_t

D → α-Fe_2O_3 + 1.0 T_t

However, in this connection it is important to refer here to the observation of Morin (1950) who found the mass susceptibility of α-Fe_2O_3 abruptly falls down from 130×10^{-6} to 19.0×10^{-6} at below 240°K (figure 2).

It is well known that the structure of glass is sensitive to temperature. It is not unlikely that at low temperature a modified structure of each glass may

also set in with an altered atomic arrangement in glass structure, where the structure of the liquid phase colours (which are part and parcel of the glass structure), also change. It is likely in the case of low temperatue glass structure that the mean moment values of some of these covalent types of iron groupings are smaller than the corresponding room temperature mean moment values. Consequently, there will be an overall decrease in the moment value with decreasing temperature

Thus a number of probable causes for the decreasing trend of moment value of iron with lowering of temperature, for each glass, have been discussed. The resultant effect may be due to one or more of the above causes. In the light of these reasonings the peculiar low temperature behaviour of iron glasses like lithia-boric oxide and high lead potash-silica glass (vide Table II) can be accounted for, particularly for the anomalous low temperature behaviour of 'solid phase' paramagnetic carriers, apart from the relative decrease due to covalent iron groupings in those iron glasses which are likely to be small from the consideration of their glass composition.

It is of interest to mention here that there is an indication of sharp fall in p^2_{eff} values of iron in all experimental samples around 240°K (figure 1). This bears a similarity with the low temperature behaviour of α-Fe_2O_3 (Morin, 1950; figure 2).

In contrast with the results on the borate and potash-lead-silica glasses, the behaviour of the boric oxide-iron glass is interesting in the sense that (1) the moment value of iron in the boric oxide glass at room temperature is very low, much lower than the moment value of Fe(ous) 'spin only' value and (2) the moment value of iron increases very slightly with the lowering of temperature. The p^2_{eff}—T values of boric oxide glasses are given in figure 1

The low moment value of iron in the B_2O_3 glasses is due to the presence in large proportion of one or more forms of iron with a small moment value, such as α-Fe_2O_3 or covalent Fe^{+2} or Fe^{+3} ion complexes, chances of the presence of any ionic groupings of iron are very remote as is evident from the consideration of the above glass. In a corresponding iron glass system like B_2O_3--SiO_2 with 80% B_2O_3 there is no singly bonded oxygen ion and the solid phase colours like α-Fe_2O_3 is the major phase (Abd-El-Moneim Abou-El-Azm). It is likely that the small moment value of iron in the B_2O_3 system is due to the presence of a large proportion of α-Fe_2O_3. Gradual rise in the moment value of iron with the lowering of temperature may be due to the single or cumulative effect of (i) the formation or increase in particle size of a form of iron with comparatively high moment value like paramagnetic Fe_3O_4, though the overall content of such form will be small in the glass composition; or (ii) the gradual increase in size of the α-Fe_2O_3 particle with the lowering of temperature which at the same time overrides the

negative effect of the temperature independent behaviour of α-Fe_2O_3. R. R. Chevallier and Mathieu(1937) have shown that the moment value of α-Fe_2O_3 increases with the size of particle. It will be interesting to mention here that the low temperature behaviour of $Fe_2O_3-B_2O_3$ samples bear a close similarity to a system of α-Fe_2O_3 contammated with TiO_2 as impurity to the extent of 1.00% Ti of the total metal atoms present, studied by Morin (1950) where the transition at 240°K disappears totally and there is a tendency for the rise of mass susceptibility value of α-Fe_2O_3 with the lowering of temperature.

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